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Carbon dioxide capture from flue gases using microalgae: Engineering aspects and biorefinery concept

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ABSTRACT

Carbon dioxide (CO_2) is one of the most important contributors for the increase of the greenhouse effect. CO_2 concentrations are increasing in the last decades mainly due to the increase of anthropogenic emissions. To reduce the effects caused by this environmental problem, several technologies were studied to capture CO_2 from large emission source points: (i) absorption; (ii) adsorption; (iii) gas-separation membranes; and (iv) cryogenic distillation. The resulting streams with high CO_2 concentrations are transported and stored in geological formations. However, these methodologies, known as carbon capture and storage (CCS) technologies, are considered as short-term solutions, as there are still concerns about the environmental sustainability of these processes.

A promising technology is the biological capture of CO_2 using microalgae. These microorganisms can fix CO_2 using solar energy with efficiency ten times greater than terrestrial plants. Moreover, the capture process using microalgae has the following advantages: (i) being an environmental sustainable method; (ii) using directly the solar energy; and (iii) co-producing high added value materials based on biomass, such as human food, animal feed mainly for aquaculture, cosmetics, medical drugs, fertilizers, biomolecules for specific applications and biofuels. Approaches for making CO_2 fixation by microalgae economically competitive in comparison with CCS methodologies are discussed, which includes the type of bioreactors, the key process parameters, the gaseous effluents and wastewater treatment, the harvesting methods and the products extracted by microalgal biomass.

Contents

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1. Introduction

The global warming is a phenomenon attributed primarily to the increase of the greenhouse gases (GHGs) in the atmosphere, specially the carbon dioxide (CO_2). The global changes associated with the temperature increase include: (i) climate disturbances (changes in the amount and distribution of the precipitation); (ii) reduction in food production; (iii) glacial melting; (iv) rise of the ocean level; (v) species extinction; and (vi) many other environmental problems that cannot be determined today [1]. This concerns led to Kyoto Protocol promotion by United Nations with the objective of reducing GHGs by 5.2% on the basis of the emissions in 1990 [2]. Many countries had difficulty to accomplish their targets, as Portugal, where the increase of GHGs emissions were limited for 2008–2012 as 27% on the basis of emissions in 1990; nevertheless, in 2008 the increase was 3% higher than they stated for 2008–2012 [3]. The energy sector was the most important source, accounting for 71.8% of the total emissions in 2008; energy industries and transports were the most important sources, representing, respectively, 24.8% and 24.9% of the GHGs emissions. Portugal presented the fourth greatest increase of GHG emissions in European Union since 1990. Thus, the study of CO_2 sequestration strategies from anthropogenic emissions is very important to accomplish the limit established by the Kyoto Protocol.

There are several strategies for capture and sequestration of CO_2. The strategies that have been intensively studied are included in the carbon capture and storage (CCS) methodologies. CCS cover three steps: CO_2 capture, CO_2 transportation and CO_2 storage. The capture is usually performed in large sources of CO_2, such as power plants and cement manufacturing facilities. Several methods can be applied with this aim: (i) absorption; (ii) adsorption; (iii) gas-separation membranes; and (iv) cryogenic distillation [4–7]. The resulting gas mixture (with high CO_2 concentration) is then compressed to a liquid and supercritical fluid to be transported by pipeline or ship [8–10] to the place where it will be stored. The storage options comprise geological storage, ocean storage and mineralization. In essence, CCS keeps CO_2 out of atmosphere by capturing it from exhaust gas and injecting it in deep reservoirs that contained fluids for thousands of years. CCS is an important technological option because it allows the societies to maintain their existing carbon-based infrastructure, while minimizes the effects of CO_2 on earth climate system. However, several technological, economical and environmental issues, as well as safety problems, remain to be solved. These procedures should only be considered as short-term solutions.

As an alternative, the biological processes can be applied to CO_2 capture [11]. CO_2 capture can be performed through enhancement of natural sinks: (i) forestation; (ii) ocean fertilization; and (iii) microalgal cultures [12]. In this review, microalgae are defined as all unicellular and simple multicellular photosynthetic microorganisms, being prokaryotes (cyanobacteria) or eukaryotes (for instance, green algae) [13,14]. The biological processes have actually an important role in the equilibrium of the atmospheric CO_2 concentration. For instance, photosynthesis occurring in the oceans is responsible for approximately 40% of the overall amount of carbon annually fixed on the planet [15]. The aquatic environment is by far the greatest active reservoir of carbon in the planet (38,000 Gt, compared with 748 Gt in the atmosphere) [16]. Thus, the microalgal culture is the biological CO_2 capture process that had detained the attention of many researchers [2,11,17]. These microorganisms have the ability to fix CO_2 using solar energy with efficiency 10 times greater than that of terrestrial plants. Moreover, the capture process using microalgae has the following advantages: (i) being an environmental sustainable method; (ii) using directly the solar energy; and (iii) producing high added value materials based on biomass, human food, animal feed mainly for aquaculture, cosmetics, medical drugs, fertilizers, biomolecules for specific applications and biofuels [18–21].

Table 1
Comparison between microalgae production in open and closed bioreactors.

Factor	Open systems (raceway ponds)	Closed systems (photobioreactors)
Space required	High	Low
Evaporation	High	No evaporation
Water loss	Very high	Low
CO_2-loss	High	Low
Temperature	Highly variable	Required cooling
Weather dependence	High	Low
Process control	Difficult	Easy
Shear	Low	High
Cleaning	None	Required
Contamination	High	None
Algal species	Restricted	Flexible
Biomass quality	Variable	Reproducible
Population density	Low	High
Harvesting efficiency	Low	High
Harvesting cost	High	Lower
Light utilization efficiency	Poor	Good
Most costly parameters	Mixing	Oxygen and temperature control
Energy requirement (W)	4000	1800
Capital investments	Low	High

Modified from Harun et al. [22], Grobbelaar [24] and Carvalho et al. [106].

This study aims to present a review of the published works about the CO_2 fixation by microalgae, their cultivation, processing and applications to be economically competitive with CCS methodologies. The topics here reported are: (i) the type of bioreactors; (ii) the key process parameters; (iii) the gaseous effluents and wastewater treatment; (iv) the harvesting methods and the products extracted by microalgal biomass; (v) the economical comparison with CCS; and (vi) the future trends of microalgal cultures.

2. Microalgal culture

2.1. Bioreactors

Microalgae can grow either in open ponds or closed systems (photobioreactors). Fig. 1 shows images of the most common bioreactor configurations. Table 1 makes a comparison between the open and closed bioreactors concerning the production of microalgae. The production in open ponds depends on the local climate due to the lack of control in this type of bioreactors. The contamination by predators is an important drawback of this cultivation system. Thus, high production rates in open ponds are achieved with algal strains resistant to severe culture environment; for instance, the *Dunaliella*, *Spirulina* and *Chlorella* spp. are cultivated in high salinity, alkalinity and nutrition, respectively [22,23]. Besides the technological simplicity, the production in open systems is not cheap due to the downstream processing costs.

Closed photobioreactors have attracted much interest by researchers, because, as contamination can be reduced, they allow better control of cultivation conditions than in open systems; consequently, higher biomass productivities can be reached [22,24]. Photobioreactors require less space; they lose less water by evaporation and CO_2 to the atmosphere. However, cooling and heating systems are required to control the cultivation temperature. Photobioreactors appear in different configurations: vertical column reactors (bubble columns or air-lift); tubular reactors; and flat-plate reactors. The air-lift reactors have great potential for industrial processes, due to low level and homogeneous distribution of hydrodynamic shear [25], which constitutes a disadvantage of closed photobioreactors to open ponds. The medium circulates in a cyclic pattern through channels built for this purpose. The

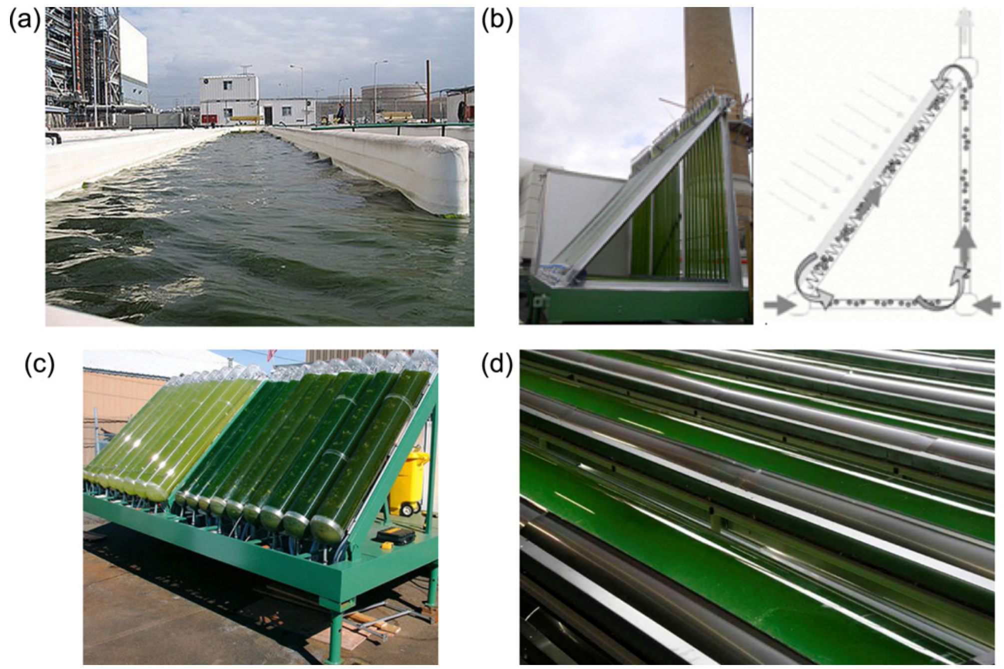


Fig. 1. Reactor configurations for microalgal cultivation: (a) raceway pond; (b) air-lift reactor; (c) bubble column reactor; and (d) horizontal tubular reactor. (a) From Seambiotic; (b) from Green Fuel Technologies – MIT, a courtesy from Vunjak-Novakovic et al. [25]; (c) from Green Fuel Technologies; and (d) from http://www.algaelink.com/.

tubular design is more appropriated to the outdoor culture, having large illumination surface created by the disposition of the tubes. They can be configured in vertical, horizontal or inclined planes. The vertical tubular reactors increase the contact time between the gaseous and liquid phases, increasing the CO_2 mass transfer [11]. However, this disposition has the disadvantage of air pumping costs. On the other hand, the flat-plate photobioreactors can achieve higher cell densities than the other bioreactors (in more than an order of magnitude). Additionally, this type of bioreactors has: (i) lower power consumption; (ii) high mass transfer capacity; (iii) no dark volumes; and (iv) high photosynthetic efficiency.

Besides the many advantages associated with closed systems, for large scale cultivation, microalgae are usually produced in open ponds due to the lower investment and production costs [23]. Despite several years of research, the major part of the microalgal world production is performed in open ponds [26].

2.2. Key growth parameters

The research on CO_2 removal by microalgae covers two fields: (i) the CO_2 capture from flue gases (10–20% CO_2) and (ii) the CO_2 capture from closed spaces (less than 1% CO_2). The process variables that could influence the success of cultivation are the light distribution and saturation, temperature, pH, salinity, nutrient qualitative and quantitative profiles, dissolved oxygen concentration and presence of toxic elements (heavy metals) [26,27].

Light supply is the most important variable that influences the growth kinetics of microalgae. The culture systems can be illuminated by sunlight, artificial light or by both. The growth rate of microalgae increases with light intensity until a certain value. Molina Grima et al. [28] presented several models relating the growth rate with light intensity. The light/dark cycle also plays an important role in microalgal growth. At high photon flux densities, the probability of photodamage (damage of protein D1 in photosystem II and consequent reduction of active "photon traps") will increase, reducing the photosynthetic activity. During the dark period, the algae could repair the photo-induced damage [29]; in this context, the design of air-lift reactors is a great advantage [25,30]. The light flux decreases exponentially with the distance from the irradiated surface. The cells near the irradiation source (downcomer/light zone) are thus exposed to a high photon density, as compared to the ones at the center (riser/dark zone), which receive less light as a result of shading.

Grobbelaar et al. [31] observed the release of oxygen from a *Scenedesmus obliquus* culture in a small volume chamber irradiated by continuous light or under different light/dark frequencies. The results demonstrated that the photosynthetic rates increased exponentially with increasing light/dark frequencies. The low light/dark frequencies were perceived by the cells as low light conditions, while the opposite was true for higher frequencies. The microalgae became progressively more efficient in the overall utilization of light energy when dark period was longer than light period. However, a longer dark period relative to light period did not mean that high photosynthetic rates can be achieved. Moreover, it was also observed that the microalgae do not acclimate to a specific light/dark cycle. The efficiency of light utilization by microalgae depended on its acclimated state, the specific frequency of the light/dark fluctuations and the duration of the exposure.

Jacob-Lopes et al. [32,33] evaluated the influence of the photoperiod on the rates of CO_2 sequestration by cyanobacteria *Aphanothece microscopica Nägeli* using standard BGN medium and refinery wastewater. Using BGN medium, a linear reduction of biomass productivity was observed with the increase of the dark period. Using refinery wastewater the photosynthetic quotient was determined, having the average value of 0.74 (1 g of CO_2 consumed corresponds to the release of 0.74 g of O_2). The intermittent light cycle had a strong influence on the gases exchange pattern. During the dark periods, the cells consumed organic carbon through heterotrophic metabolism, consuming O_2 and releasing CO_2.

The microalgal growth can be improved through sequential change of light intensity. The irradiance should be regulated according the culture density. For lower culture densities, high light intensities can cause photoinhibition and for high culture densities, the light penetration is limited (increasing the dark volumes). Thus,

the intensity of light supplied should increase progressively with the increase of the culture density. This methodology was applied to *Neochloris oleoabundans* in batch photobioreactors [34]. In this study, the biomass concentration doubled in sequential change of light intensity when compared with constant light.

The distribution of light in photobioreactor has a key role in its design [26,27,35]. The solar irradiation could be collected and concentrated into optical fibbers with lenses or parabolic mirrors. The optical fibbers can guide the light into large scale photobioreactors. Fig. 2 shows a concept of microalgal production using optical fibbers [36]. This photobioreactor design increases the electrical energy efficiency (for artificial illumination), enhancing light distribution in the medium (for artificial or natural illumination) and minimizing the ratio between occupied surface and photobioreactor volume (great disadvantage of this CO_2 capture technology). Jinlan et al. [37] designed a novel photobioreactor with parallelepiped body divided in five compartments. The optical guides, disposed perpendicularly into compartments, are able to diffuse light laterally and ensure its homogeneous distribution in the medium. The performance of a light diffusing optical fibber photobioreactor was also evaluated for high density culture of marine cyanobacteria *Synechococcus* sp. [38,39]. High CO_2 removal and biomass production rates were achieved with this type of reactors; however, the use of optical fibbers is a costly solution, being possible to apply for production of high-value compounds.

As referred above, one of the main applications for microalgal culture is the CO_2 capture from flue gases. Direct supply of flue gas in the photobioreactor reduces the pre-treatment costs, but imposes extreme conditions for microorganisms, such as high concentrations of CO_2, presence of inhibitory compounds (like NO_x and SO_2) and high temperatures. The response of microalgae to the first two environmental conditions is described in more detail in the next sections. The supply of gases such CO_2, NO_x and SO_2 reduces the pH of the culture medium. Maeda et al. [40] added $CaCO_3$ to medium to prevent the drop in pH and consequent microalgae death (no problem was observed in their experiences). Usually, the microalgae grow at temperatures ranging 25–35 °C. Several researches were performed to identify thermal-tolerant strains able to fix CO_2 at high temperatures: (i) *Chlorella sorokiniana* UTEX-1230 at 42 °C [41]; (ii) *Chlorella* KR-1 at 40 °C [42]; (iii) thermophilic cyanobacteria *Chlorogleopsis* sp. at 50 °C [43]; and (iv) two thermal-tolerant mutants of *Chlorella* sp. MT-7 and MT-15 at 40 °C [17].

Another key issue in microalgal culture is the mass transfer, especially for CO_2 and O_2. As CO_2 has a low mass transfer coefficient, the mass transfer from gaseous to liquid phases is the major limiting step in cultivation of photosynthetic microorganisms [44]. The oxygen produced by photosynthesis inhibits the microalgal growth, when this gas is present in high concentrations. A common solution to reduce this negative effect is to supply the gas with high flow rates or working in turbulent regime [45]. This procedure enhances the mass transfer and homogenizes the medium (homogeneous distribution of heat, cells and the different compounds of the medium). Additionally, higher flow rates led to shorter light/dark cycles (with frequency fluctuations greater than 1 Hz), increasing the biomass production. However, the high turbulence can damage cells due to the shear stress and increase power consumption. Cheng et al. [46] evaluated the performance of a photobioreactor with a hollow fibber membrane for CO_2 fixation by *Chlorella vulgaris*, aiming the enhancement of CO_2 and O_2 mass transfer. The membrane was used for CO_2 supply and for removing the oxygen produced by photosynthesis. The CO_2 fixation capacity increased more than 3 times when the membrane was applied. However, this process has a drawback of fouling deposition, which increases the pressure drop, reducing the mass transfer and increasing the consumed power for gas transport.

2.3. CO_2 fixation rates

Microalgal photosynthesis is efficient enough to fix CO_2 in both atmosphere and industrial flue gases. Their capture capacity is about ten times higher than terrestrial plants. These microorganisms can accumulate inorganic carbon in their cytoplasm to concentrations several orders of magnitude higher than that on the outside, phenomenon called CO_2-concentrating [47–49]. Several CO_2 concentrations were supplied to bioreactors to evaluate the microalgal behavior. CO_2 concentration is an important parameter for photosynthesis. High concentration increases CO_2 mass transfer from the gas mixture to the medium (a limiting step of CO_2 fixation by microalgae), but the consequent pH reduction inhibits the growth of some microalgal species. However, as flue gases present high CO_2 concentrations, several studies were performed to identify high CO_2-tolerant microalgal species [41,50]. It should be remarked that the supplied CO_2 should never fall below a minimum that limits the photosynthesis and consequent microalgal growth. Another important microalgal growth inhibitor is the O_2 produced by photosynthesis, which should be removed to avoid high medium concentrations of this gas. Jacob-Lopes et al. [15] described O_2 removal in photobioreactors using a first order kinetics model.

Table 2 shows CO_2 fixation rates for several cultures of microalgae under different operational conditions. These values can be used to estimate the area needed for the reactor implementation for CO_2 fixation. For instance, the Portuguese cement industry *Secil* produces annually about 450 kt of CO_2 and has been testing a pilot-scale tubular reactor with the cooperation with *AlgaFuel Company* [51]. Considering two reactors, open ponds (the most used in world microalgal production) or light-diffusing optical fibber (LDOF) reactors (one of the most promising reactors due to high surface area:volume ratio, greater energy efficiency and improved scale-up properties), the estimated areas are very different. Studies reported that a 4000 m^3 open pond could sequester up to 2.2 kt of CO_2 per year, under natural daily light exposure cycles [11]. If the scaling up is plausible and the open ponds height is 30 cm (to reduce dark zones), open ponds occupying an area of 2.72×10^6 m^2 are needed to sequester the CO_2 emitted by *Secil* industry. For LDOF reactors, the reported CO_2 fixation rate was 4.44 $g\,L^{-1}\,d^{-1}$ [39]. Considering the reactor height of 1 m (the light is conducted more deeply by the optical fibbers), a culture area of 2.78×10^5 m^2 (more the area occupied by the optical fibbers) is needed, which represents a significant reduction in this important process parameter.

2.4. Effect of NO_x and SO_2

Flue gases are the gas mixtures with more interest for CO_2 capture using microalgal cultures. However, it contains not only CO_2, but also sulfur and nitrogen oxides. These compounds may be toxic for the cultures growth by reducing the solution pH and also by direct inhibition. Negoro et al. [52] evaluated the SO_x and NO_x effects on the growth of ten strains of marine and halotolerant microalgae. With CO_2 concentration of 15%, the growth of *Nannochloris* sp. and *Nannochloropsis* sp. was not affected by 50 ppm of SO_2. However, at 400 ppm of the same gas, the pH dropped and the growth stops after 20 h of cultivation. The same strains were tested with high level of CO_2 and 300 ppm of NO. Despite of the absence of a significant change of pH value, both growths were affected by this air pollutant. *Nannochloropsis* sp. did not grow while *Nannochloris* sp. grew after a prolonged lag period. Hauck et al. [53] tested *C. vulgaris* and *Cyanidium caldarium* for CO_2 capture in a simulated flue gas (with NO_x and SO_x). *C. caldarium* was selected due to its ability to grow in highly acidic media and at elevated temperature, which is an advantage above the other species for CO_2 capture

Table 2
CO_2 fixation rates using several microalgal strains cultivated in different bioreactors.

Reactor		Microalgae species	Supplied CO_2 (%)	Temperature (°C)	pH	Light conditions		Growth rate (d^{-1})	CO_2 fixation		Refs.[d]
Type	Vol. (l)					Intensity	Photoperiod		Rate	Efficiency (%)	
Open pond reactors	8	*Spirulina platensis*	10	30	10	30^{c1}	12:12			39	1
	8	*Chlorella sp.*	10	30	10	30^{c1}	12:12			46	2
	330	*Chlorella sp.*	6–8			Sunlight				50	3
Bubble column reactors	0.2	*Chlorella vulgaris*	15	27		110^{c2}	24:0		0.62^{c5}		4
	0.3	*Chlorella sp.*	40	42	7.9	500^{c2}		5.76			5
	0.5	*Chlorella vulgaris*	10–13	30	6.5–7.5	1150^{c2}			4.4^{c5}		6
	0.6	*Chlorella sp.*	5			100^{c1}			0.58^{c5}		7
	0.8	*Chlorella sp.*	2	26 ± 1		300^{c1}			7.83^{c5}	58	8
	0.8	*Chlorella sp.*	5	26 ± 1		300^{c1}			9.48^{c5}	27	9
	0.8	*Chlorella sp.*	10	26 ± 1		300^{c1}			14.0^{c5}	20	10
	0.8	*Chlorella sp.*	15	26 ± 1		300^{c1}			17.2^{c5}	16	11
	1	*Thermosynechococcus sp.*	10	55		10,000 ± 350^{c3}	24:0	2.7			12
	1.6	*Chlorella vulgaris*	0.2		9 ± 0.5	40–50^{c1}			1.53^{c5}	74	13
	1.8	*Anabaena sp.*	air	27	8.5	900^{c2}			1.45^{c5}		14
	2	*Aphanothece m. Nägeli*	15	30		150^{c1}	24:0		26.9^{c5}		15
	2.4	*Aphanothece m. Nägeli*	15	25		150^{c1}	12:12		13.0^{c5}		16
	3	*Aphanothece m. Nägeli*	15	35		11,000^{c3}	24:0		2.621^{c5}		17
	3	*Aphanothece m. Nägeli*	15	35		150^{c1}			1.44^{c5}		18
	5.4[a]	*Spirulina sp.*	6	30		3200^{c3}	12:12			37.9	19
	8	*Dunaliella tertiolecta*	5	25	7.2 ± 0.2	3500^{c3}	12:12		0.272^{c5}		20
	8	*Chlorella vulgaris*	5	30	7.2 ± 0.2	3500^{c3}	12:12		0.252^{c5}		21
Bubble column reactors	8	*Spirulina platensis*	5	30	9.0 ± 0.2	3500^{c3}	12:12		0.319^{c5}		22
	8	*Botryococcus braunii*	5	25	7.2 ± 0.2	3500^{c3}	12:12		0.497^{c5}		23
	10[b]	*Chlorella vulgaris*	1	25–30		157.6^{c2}	12:12		6.24^{c5}		24
Air-lift reactors	1.1	*Synechococcus sp.*	5	30	6.8	8000^{c3}			0.6^{c5}		25
	2.4	*Aphanothece m. Nägeli*	15	25		150^{c1}	12:12		14.5^{c5}		26
	4	*Chlorella sp.*	10	26 ± 1		300^{c1}		0.252		63	27
Tubular reactors	12.1	*Spirufina platensis*	4	36 ± 2		2920^{c4}				70	28
Flat-plate reactors	11.4	*Chlorococcum littorale*	5	25	6.1–7.2	2000^{c1}			200.4^{c6}		29
	72	*Synechocystis aquatilis*	10	40 ± 3		Sunlight			51^{c6}		30
LDOF reactor	2.5	*Synechococcus sp.*	0.55			50^{c2}			4.44^{c5}		31
Other reactors	1.8	*Scenedesmus obliquus*	12	30		3200^{c3}	12:12	0.261			32
	1.8	*Chlorella kessleri*	6	30		3200^{c3}	12:12	0.267			33
	100	*Euglena gracilis*	5–10	27	3.5 ± 0.1	178.7^{c1}			0.074^{c5}		34

Blank indicates no information available.

[a] Three-stage serial bubble column reactor (3 × 1.8 l).

[b] Bubble column reactor with membrane.

[c1] In $\mu mol\ m^{-2}\ s^{-1}$.

[c2] In $\mu E\ m^{-2}\ s^{-1}$.

[c3] In lux.

[c4] In $kJ\ d^{-1}$ (PAR, 400–700 nm).

[c5] In $g\ l^{1}\ d^{-1}$.

[c6] In $g\ m^{-2}\ d^{-1}$.

[d] Refs.: 1 – [107]; 2 – [107]; 3 – [108]; 4 – [61]; 5 – [41]; 6 – [109]; 7 – [110]; 8 – [111]; 9 – [111]; 10 – [111]; 11 – [111]; 12 – [44]; 13 – [112]; 14 – [113]; 15 – [33]; 16 – [114]; 17 – [115]; 18 – [32]; 19 – [116]; 20 – [117]; 21 – [117]; 22 – [117]; 23 – [117]; 24 – [46]; 25 – [65]; 26 – [114]; 27 – [118]; 28 – [119]; 29 – [120]; 30 – [121]; 31 – [39]; 32 – [122]; 33 – [122]; 34 – [123].

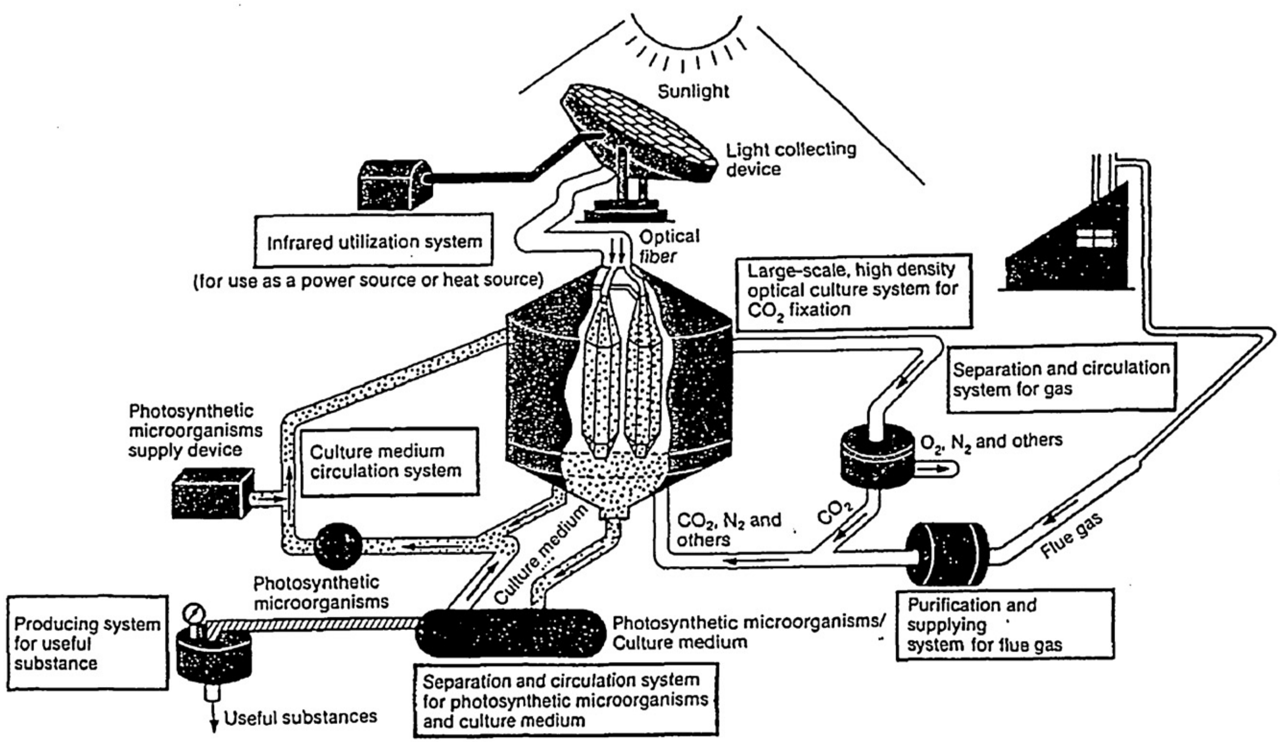


Fig. 2. A concept of microalgal production using optical fibbers.

A courtesy from Michiki [36].

from flue gas. This alga showed to be able to grow at temperatures above 57 °C and lower pH values. On the other hand, the growth of *C. vulgaris* was completely inhibited when the flue gas contained 200 ppm SO_2, 15% CO_2 and 3% O_2 in N_2 stream.

The elimination of SO_x from the flue gas can be performed using a chemical desulfurization system. However, to remove NO is more difficult due to its lower solubility in the liquid phase. Considering this difficulty, Yoshihara et al. [54] cultivated the marine microalgae NOA-13, trying to eliminate NO and CO_2, simultaneously. Using a 4 dm^3 reactor column with aeration of 300 ppm (v/v) NO and 15% (v/v) CO_2 in N_2 at a rate of 150 $cm^3\,min^{-1}$, about 40 mg of NO (half of the NO supplied) and 3.5 g of CO_2 were eliminated per day. Nagase et al. [55–57] investigated the potentiality of the microalga *Dunaliella tertiolecta* to remove NO_x from fuel flue gas; NO, the main component of NO_x in flue gases (more than 90%), was supplied with concentration ranging from 25 to 500 ppm, being removed about 65%. The elimination of NO was associated to the presence of both microalgae and oxygen. Applying various culture conditions, it was concluded that the dissolution in aqueous phase is the rate-limiting step in the reactor system. NO elimination was evaluated in bubble column and airlift reactors. The highest level of NO removal was achieved with a counter-flow type airlift reactor (three times higher than the one obtained in a simple bubble column reactor) when smaller bubbles of NO at 100 ppm were supplied. This procedure enhances the mass transfer of NO, increasing the transfer area and the concentrations gradient (the driving force of mass transfer of NO from gaseous to liquid phase). The NO uptake pathway was described. NO in the gaseous phase dissolves in the medium and it is taken by algal cells by diffusion. It was observed that the consumption of nitrates dissolved in the medium was reduced when NO was supplied to the culture. Therefore, the cells used preferentially NO as a nitrogen source rather than nitrates.

Santiago et al. [58] evaluated the effects of the addition of Fe(II)EDTA to microalgae *Scenedesmus* sp. on NO removal. The results showed that this compound enhances the NO fixation at a level higher than the one obtained with bacterial denitrification systems.

2.5. Use of wastewater

The combination of CO_2 fixation from flue gas and nutrient removal from wastewater may provide a very promising alternative to current CO_2 capture strategies; it is also another important environmental benefit of these microorganisms. Microalgae can utilize low-quality water, such as agricultural runoff or municipal, industrial or agricultural wastewaters, as a source of water for the growth medium as well as a source of nitrogen, phosphorus and minor nutrients [2,59,60]. These nutrients are directly responsible for eutrophication of rivers, lakes, and seas.

Yun et al. [61] cultivated *C. vulgaris* in wastewater discharged by steel-making plant to develop an economically feasible system to remove ammonia from wastewater and CO_2 from flue gas, simultaneously. The selected strain utilized preferentially the ammonia rather than nitrate as nitrogen source. The nitrate was not consumed until the ammonia in wastewater is exhausted. As the used wastewater did not have phosphorus compounds, external phosphate was added to wastewater. Moreover, to improve the microalgal growth using the flue gas with 15% (v/v) of CO_2, a period of adaptation was needed in which a gas mixture with 5% (v/v) was supplied to the culture. The CO_2 fixation and ammonia removal were 26.0 $g\,m^{-3}\,h^{-1}$ and 0.92 $g\,m^{-3}\,h^{-1}$, respectively.

Chinnasamy et al. [62] cultivated native mixotrophic algal strains (*Chlamydomonas globosa*, *Chlorella minutissima* and *Scenedesmus bijuga*) in untreated wastewater of carpet industry, using raceways, vertical reactors and polybags. In all bioreactors, a gas stream with 5–6% of CO_2 was supplied. Biomass productivity was 21.1 $g\,m^{-2}\,d^{-1}$ for polybags, 8.1 $g\,m^{-2}\,d^{-1}$ for vertical tank reactors and 5.9 $g\,m^{-2}\,d^{-1}$ for raceways.

Jacob-Lopes et al. [33] evaluated the global rates of CO_2 fixation by cyanobacteria *A. microscopica Nägeli* in refinery wastewater.

The influence of the photoperiod was evaluated. The intermittent light regime had a strong impact on CO_2 fixation, resulting in a loss of 78%. In absence of light, the cells assimilated the organic carbon presented in the refinery wastewater through heterotrophic metabolism. Thus, in this period, CO_2 was released and O_2 was consumed.

Wang et al. [63] cultivated *Chlorella* sp. in wastewater sampled from four different points of the treatment flow of a local municipal wastewater treatment plant and evaluated its potential for elimination of nitrogen, phosphorus, chemical oxygen demand and metal ions. The cells grew well in all of the four wastewaters, having the highest growth rate with high levels of nitrogen, phosphorus and chemical oxygen demand. The growth was not affected by the ratio between the nitrogen and phosphorus quantities presented in wastewaters, being important the abundance of both nutrients. The microalgae removed efficiently the metal ions Al, Ca, Fe, Mg, and Mn.

3. Harvesting methods

The main constraint to microalgal production is the cost, the harvesting process representing more than 20% of the total [64–66]. The dilute nature of microalgal culture contributes for the increase of energy demand for dewatering process, especially for industrial scale. Conventional methods for harvesting are centrifugation, filtration and flocculation, either used individually or in combination [67]. However, most of these methods still involve economic or technological drawbacks, such as a high energy cost (centrifugation), algal biomass contamination (chemical flocculation), or non-feasibility of scaling-up [68,69]. Molina Grima et al. [70] presented an interesting and complete review about the referred microalgal harvesting methods. Besides the operational cost, concerning selection of the adequate harvesting method, several aspects should be considered: (i) harvesting speed; (ii) harvesting efficiency; and (iii) density and quality of biomass in the resultant concentrate [65].

Centrifugation is a solid–liquid separation process, which uses the action of centrifugation force to promote accelerated settling of particles dissolved in the liquid. It is a method that has been applied successfully for harvesting microalgae, as it processes rapidly large volumes presenting high biomass recovery. However, it shows several disadvantages [66,67,71–73]: (i) cells are exposed to high gravitational and shear forces, which can damage the cell structure; (ii) biomass recovery of microalgae with fragile structure needs low velocity of centrifugation; and (iii) large volume processes require expensive equipments (continuous centrifuges) increasing operational costs. Thus, centrifugation is only suitable for high value products [67,70]. For recovery of marine microalgal biomass, the presence of salt increases the corrosion speed, which means that centrifugation is not an economical method for harvesting from saline media.

Filtration is a physical separation process, which is used to separate particles (solids) and fluids in a suspension by a filter (membrane): the fluid passes through these filters and the solids are retained. Membranes are characterized by their efficiency, reliability and safety for the solid–liquid separation. However, concerning the microalgal harvesting, the biomass recovery may be unsatisfactory, as it is a relatively slow process [70]. The main limitation is the progressive fouling, responsible for the reduction of permeation flux during the separation process. The principle causes can be adsorption, concentration of compounds on surface and eventually pore clogging [74,75]. The methods applied to reduce the impact of fouling phenomena are: (i) the application of cross-flow rather than frontal filtration; (ii) working with high velocities; and (iii) selecting a design that induces instability near the membrane surface. Zhang et al. [76] characterized the fouling achieved in the recovery of microalgal biomass. The adsorption of algogenic organic matter was the main responsible for membrane fouling. The authors also proposed a solution for fouling removal, based on the addition of NaClO. Another drawback of filtration is the shear stress of microalgal cells during the harvesting process (as it happens with centrifugation). Therefore, for microalgae with fragile structures, a suitable pumping system should be selected [69,77].

A widely used membrane technique for cell harvesting is the tangent flow filtration (TFF) process [64,69,74,77–79]. In TFF (such as microfiltration or ultra-filtration), the bulk flow is parallel to the filtering membrane and perpendicular to the permeation flux. Danquah et al. [78] compared TFF with flocculation for the dewatering of *Tetraselmis suecica* microalgal culture. Besides presenting lower solid concentration and higher initial capital investment, TFF presented a reduced payback period (approximately 1.5 years) when compared with flocculation (approximately 3 years).

Flocculation is a process where particles in a liquid settle to the bottom of a tank due to the gravitational force and fluid drag force [80]. Flocculation can be achieved in different ways: (i) chemical flocculation; (ii) bio-flocculation; or (iii) electro-flocculation. Flocculation is a preferred method to harvesting large cells (microalgae), as it is a simple and fast process and presents lower costs compared with other harvesting methods. This process is already used in industry for clarification of wastewater treatment [81–83], clarification of drinking water [71,84], color removal in papermaking industry and mineral processing [85]. The flocculation of microalgal biomass is particularly sensitive to the pH, properties of the cellular surface, concentrations of the flocculants and divalent cations and ionic strength of the culture solution, between other factors [68]. The common applied flocculants are aluminum sulfate, aluminum and ferric chlorides [86,87]. The addition of NaOH solution, increasing the pH of the culture to 8–11, can coagulate and settle suspended cells in few minutes [71,88]. The biomass is recovered by gravity sedimentation. This harvesting process achieves efficiency greater than 90% and biomass density of 15 g/l (these results were obtained in separation of cells with halotolerant characteristics) [88]. Besides high cell recovery, this process has several advantages: (i) operational simplicity; (ii) cheap running costs (NaOH is cheaper than the flocculant); and (iii) reuse of the clarified culture broth. The selection of the adequate flocculant depends on the aim of the separation process [72]. For production of biodiesel, the efficiency and economy are important. In this process, the selection must focus in the fastest and cheapest flocculant, which is aluminum chloride.

However, the referred flocculants are toxic when consumed at high concentrations. Ideally, the flocculants used should be inexpensive, nontoxic, and effective in low concentration. In addition, the flocculant should be selected so that further downstream processing is not adversely affected by its use. Therefore, several studies [67,68,89] concerned about alternative flocculants for microalgal harvesting to avoid the biomass contamination. Chitosan, an organic cationic polymer, is a non-toxic flocculating agent already applied in wastewater treatment and food industry. Besides its non-toxicity, it is easy to manufacture and only a few dosage is required for microalgal harvesting [66]. Although chitosan is more environmental friendly than polyelectrolyte flocculants, it is still not economical for microalgal separation due to its higher price. However, other flocculants were tested, some of them that already presented good results in other solid–liquid separation processes. It is the case of cationic starch that is applied in wastewater treatment and paper mill industries. Vandamme et al. [66] tested this flocculant for harvesting freshwater microalgae, presenting lower needed dosage when compared to inorganic flocculants. Cationic starch has lower number of functional groups than chitosan (higher

needed dosage). On the other hand, chitosan is more expensive and it is not available in large volumes.

Microbial flocculation is an interesting alternative to other harvesting methods, as it presents lower costs and avoids the biomass contamination with metallic ions (used in chemical flocculation) [67,68,89]. Organic carbon, such as acetate, glucose or glycerin, is used as substrate for the growth of flocculating microbes in situ. Under nutrient stress, these microbes produce extracellular polymeric substances that promote the flocculation of the cells in the culture. For the production of biodiesel from microalgae, the organic substrate is available (e.g. glycerin is a by-product of biodiesel production). Moreover, at larger scales, the culture media could be reused to minimize the cost of nutrients and the demand of water. However, it requires the mixing of high volumes of algal cultures and therefore the estimation of the involved energy is necessary. Lee et al. [89] designed a bioflocculator and estimated that 0.893 kWh of mixing energy per 103 kg of dry mass flocculated is required. Besides bio-flocculation, electro-flocculation also presents lower costs and avoids biomass contamination. This technique does not use flocculants, needing relatively small amount of electric energy (0.3 kWh m^{-3}) to flocculate the microalgae [90]. It can be applied to several groups of microalgae achieving biomass recoveries greater than 90%, the control being relatively easy.

4. Biomass applications

After harvesting, the microalgal biomass is dried using one of the following processes: sun or spray-drier. In the final state, the product is in powder or in compressed form as pastilles. Considering the chemical composition of microalgae, their biomass could have several applications: human food, animal feed mainly for aquaculture, cosmetics, medical drugs, fertilizers, biomolecules for specific applications and biofuels. For different microalgal species, their composition in lipids, proteins and carbohydrates varies widely. The lipid content varies between 1% and 70% and the microalgal strains with high lipid productivity were intensively studied in the context of biodiesel production [13,91–93]. Some of the fatty acids are from ω-3 and ω-6 families, which are of particular interest. Considering diverse chemical properties, microalgae can act as human nutritional supplement. They contain several important vitamins (A, B_1, B_2, B_6, B_{12}, C, E). The microalgae are also cultivated for animal feed, in special for aquacultures. Concerning the pigments, microalgae is an important source of carotenoids. There are several reviews describing the applications for microalgal biomass [20,21].

4.1. Non-fuel applications

Microalgal non-fuel products can be divided in different categories: (i) human nutrition; (ii) animal feed and aquaculture; (iii) cosmetics; (iv) pharmaceuticals; and (v) chemicals.

Microalgae are good protein sources due to their high content and the amino acid pattern [21]. As the cells are capable of synthesizing all amino acids, they can provide the essential ones to humans and also animals. Concerning carbohydrates, they can be found in the form of starch, glucose, sugars and other polysaccharides. Microalgae also contain ω-3 fatty acid, which can be purified to provide a high value food supplement. This product is often obtained from fish oil, but in recent years, problems with poor oxidative stability of fish oil make it less favorable [22]. The functional sources of ω-3 in microalgae are normally eicosapentanoic acid (EPA) and decosahexaenoic acid (DHA). EPA has incredible anti-inflammatory effects, which prevents and relieves painful symptoms of arthritis. EPA has superior lipid management properties, lowering cholesterol and contributing to heart and cardiovascular health. EPA is also thought to have strong neuro-protective properties, positively affecting mental conditions such as schizophrenia and depression.

Microalgae provide good animal overall nutrition due to its blend of proteins, carbohydrates and vitamins. In aquaculture, they can be used for culturing several types of zooplankton that feed crustaceous and fish. Regarding to cosmetics, microalgae extracts is used in face and skin care products: (i) anti-aging cream; (ii) refreshing or regenerative care products; and (iii) emollient and an anti-irritant in peelers [21].

4.2. Fuel applications

Microalgae can provide several types of renewable fuels. Biodiesel is a biofuel that has physical and chemical properties similar to fossil diesel, being used for its substitution [94–96]; it is the energy product that is mostly associated with microalgal research. There are several studies referring the viability of its production using microalgae [18,92,97–101]. Biodiesel is currently produced using vegetable oils and animal fats [94,95]. However, these sources are not sufficient to produce fuel enough to satisfy the world energy demand. Additionally, the competition between energy and food markets reduced the used amounts of several raw materials for biodiesel production. In this context, microalgae can solve this energetic problem as they grow extremely rapid and many of them are rich in oil (microalgal oil productivity is about 100 times higher when compared with soybean) [97]. Some microalgal species have a convenient fatty acids profile that allows a biodiesel production with high oxidation stability. Despite being technically feasible, biodiesel production needs to improve economical competitiveness, namely concerning microalgal biodiesel.

Hydrogen is currently produced from non-renewable sources; some of the production processes are steam reforming of natural gas, gasification of coal and electrolysis of water. Nevertheless, biohydrogen can be produced from microalgae through environment-friendly methods; green alga *Chlamydomonas reinhardtii* was already tested with this aim through an aerobic-anaerobic cycle developed by Melis et al. [102]. This process (biophotolysis) is attractive as it uses sunlight to convert water to hydrogen and oxygen. However, it must achieve an overall 10% solar energy conversion efficiency to be competitive with other alternative sources of renewable hydrogen, such as photovoltaic-electrolysis processes [103].

Other important microalgal energy product is methane. The production of biogas from biomass is gaining relative magnitude worldwide. The main limitation of this energy production process is the availability of biomass. A 500 kW biomethane production plant requires about 10–12 thousand tons of biomass per year [100]. With efficiency of biomass production 5–30 times higher than crop plants, microalgae can also be used for methane production. The use of methane or biodiesel as energy source will release CO_2 again. However, the application of microalgae biomass can displace the use of fossil fuel and, consequently, this can lead to reduction of CO_2 emissions. Fig. 3 shows the paths for the different energy products that can be produced by microalgae (adapted from Oilgae [104]). The referred chemical processes are described by Amin [105].

5. Economical comparison with CCS methodologies

The comparison of methodologies for CO_2 capture should take into accounts of all important inputs and outputs to evaluate correctly the most economical solution. The CCS methodologies require energy for capture (to rise temperature or pressure in regeneration processes), transport and storage. The carbon capture should result in a relatively pure stream of gas to reduce the costs

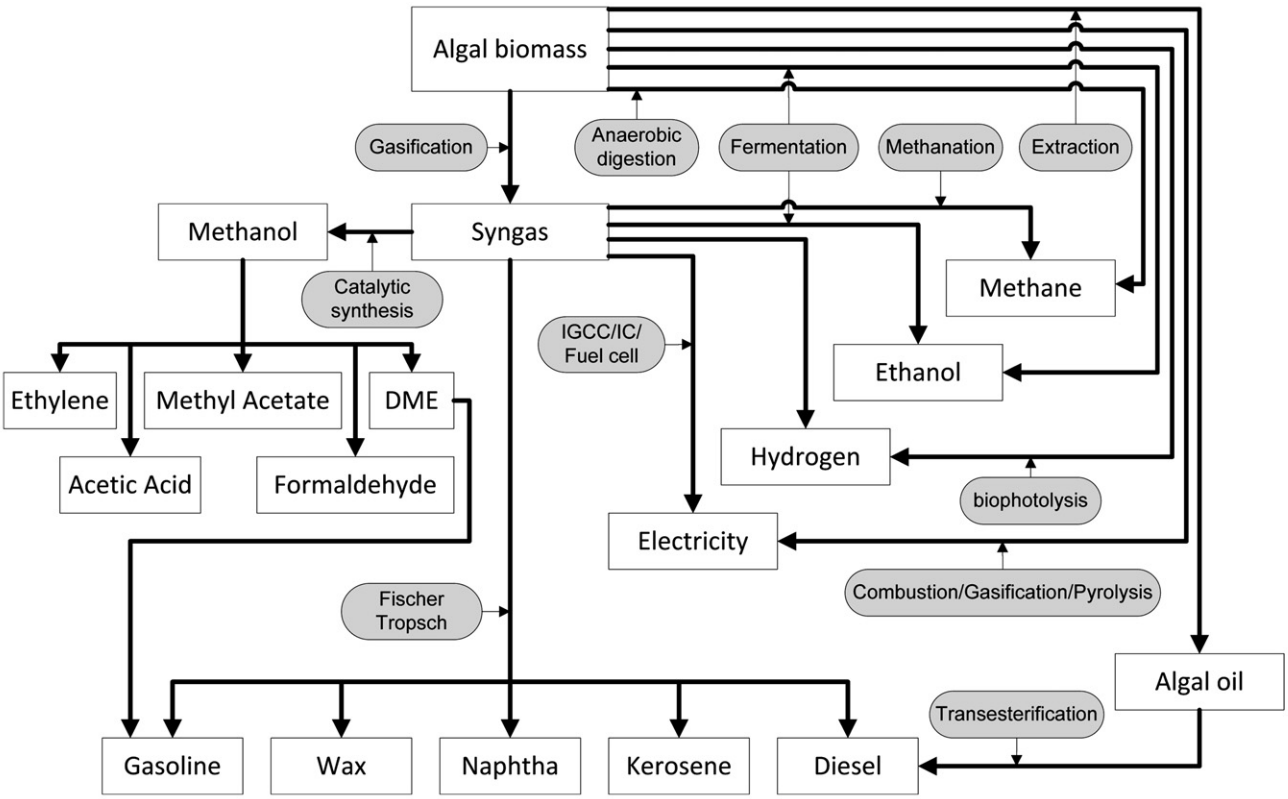


Fig. 3. Paths to several energy products from algae.

Adapted from Oilgae [104].

in transport and sequestration. As the concentrations in industry emissions are relatively low, the cost of capture is significant [11], depending on CO_2 concentration in the flue gas and on the used chemical process. The cost of transportation and storage should be about US \$5–\$15 t^{-1} of CO_2 avoided. For CCS methodology, there is not any valuable product to balance other costs. Considering the carbon cost established by Kyoto protocol for 2010 (\$270 t^{-1}), the CCS methodologies are not economically feasible; only a carbon cost of \$330 t^{-1} was assumed to make CCS competitive [11]. Additionally, CCS methodologies will have the opposition of the populations near the storage places, due to the possible CO_2 leakage (the oceanic and geological storage only delays the release of CO_2 to the atmosphere) and consequent environmental damages.

On the other hand, the CO_2 capture by microalgae also has high costs (energy for pumping the medium, compressing air, harvesting biomass, etc.), but this process has also benefits: (i) CO_2 conversion to biomass; and (ii) production of valuable products. As this process is under development, there is not a economical evaluation to estimate the cost of CO_2 capture. However, aiming the production of energy products, Posten [26] defined €40 m^{-2} as the maximum investment costs for economical design of bioreactors, but available reactors cost several times this value. Nevertheless, several authors [2,33,61] considered that the combination of CO_2 fixation, treatment of gaseous effluents and wastewater and biofuel production by microalgae cultivation provides a very promising alternative to current CO_2 capture strategies.

6. Future trends and perspectives

CO_2 capture using microalgae is a promising technology to solve the environmental problem concerning the increase of GHGs concentrations in the atmosphere. To be economically competitive with CCS methodologies, an intensive research is needed to integrate all microalgal culture benefits: flue gas and wastewater treatment and biomass production. In an environmental point of view, systems of microalgal cultures should be studied to capture CO_2 consuming the nutrients in wastewaters, simultaneously. In an engineering point of view, the costs associated with all different processes should be reduced. For instance, harvesting and dewatering are processes with high energy requirements mainly because of small cell size and low cell biomass levels in microalgal cultures; thus, research efforts should be performed to achieve high cell densities. This limitation is related with the access of the cells to gas and light. Air-lift bioreactors with light distribution through optical fibbers (increasing the ratio between the illumination surface and reactor volume) may be the solution. Apart from the advances in photobioreactor engineering, the application of the biorefinery concept (to exploit the full potential of commercial products derived from microalgal biomass) can make this CO_2 capture process economically feasible.

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